

SULFUR IMPACT ON COAL-FIRED GAS TURBINES

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ABSTRACT

Solar Turbines Incorporated is conducting a DOE-sponsored program to develop coal-fired cogeneration gas turbines. Solar's approach emphasizes the direct combustion of coal in both dry pulverized form, as well as a coal-water slurry, using a rich-lean, two-stage slagging combustor (TSSC). Under TSSC conditions, H_2S is formed in the atmosphere surrounding burning particles, and may persist in the rich zone, but the dominant sulfur species in the exhaust gas of the lean secondary zone is SO_2 . A sulfur distribution based on TSSC combustion of eastern Kentucky bituminous coal showed that up to 90% of the sulfur was converted to oxides while the remainder combined largely with the ash. The studies made to date have also indicated that over 50% of the alkalis introduced with this coal have been retained with the slag in the primary combustion zone.

INTRODUCTION

Sulfur is one of the key elements in coal fuel specifications which requires particular attention. Emissions of sulfur oxides as well as the condensation and/or deposition of corrosive sulfates on blades are major problems in the development of coal-fired gas turbines. Substantial sulfur removal will be needed in order to meet environmental standards and to reduce the interaction between sulfur and alkali compounds. Several processes exist so that clean-up of sulfur is feasible, but they are expensive. Economic considerations will continue to force greater usage of minimally cleaned coal (i.e., coal with high ash and/or sulfur content). An understanding of the role of sulfur during coal combustion and its impact on gas turbines will benefit control of sulfur emissions and corrosion. This paper reviews the role of sulfur in two-stage slagging coal combustion and discusses its impact on coal-fired gas turbines.

EXPERIMENTAL

Combustion tests were performed using a two-stage slagging combustor shown in Figure 1. The following test procedure has been used for all combustor tests conducted in this study. The combustor was started using #2 diesel to light off and establish the desired test conditions. When the wall temperatures were stabilized, a gentle transition to the coal-water mixture was accomplished by turning on the coal fuel and turning off the diesel until the combustor was operating on coal-water mixture only.

In Solar's two-stage slagging combustor, the coal fuel is injected via a series of angled injectors with air into the primary zone where the fuel-rich coal combustion takes place rapidly. The reacting jet flow impinges on the primary centerline and is then constrained by the impact dome and the refractory-lined walls to reverse and exit between the incoming flows. A strong toroidal vortex is formed surrounding the main jet and this acts primarily

as a particle retaining system. Particles smaller than some critical size follow the flow streamlines and escape. Other particles, which are larger than some upper limit, are deposited and form slag on the dome and walls. The molten slag is then collected in a slag pit.

The exhaust raw gases from the primary zone which are relatively free of particles pass into the secondary zone where remaining, unburned chars are then mixed with secondary air where combustion is completed to form desirable combustion products. The hot gas leaving the combustor enters a separator to separate particulate fly ash. Reaction temperature at the primary zone is above 2700°F with estimated temperature in secondary zone of 1600 to 1800°F.

Two coal-water fuels were formulated with high volatile bituminous, eastern Kentucky coals (Kentucky #5 and Elkhorn #2 mines) from AMAX Extractive R & D. Fuels were obtained in the form of aqueous slurries and prepared by physical beneficiation. Coals were cleaned in a static-bath dense-medium separator for refusing sinks and collecting clean coal floats. The float coals typically contained less than 3.9% ash and had calorific heating-values above 14,400 Btu/lb on a dry basis. Stable, pumpable slurries of coal and water were prepared by grinding the dense-medium float coal further in a ball mill to achieve a desired particle size. The finish-ground slurry was blended to with 1.2 to 1.4% of dispersant. A list of fuel properties appears in Table 1.

TABLE 1

Coal-Water Slurry Fuel Characteristics

CWM Batch	A	C
Coal Content of Fuel (wt%)	59.98	54.1
Ash Content of Fuel (st%)	1.85	2.1
Coal Particle Top Size (micron)	.44	100
Gross Heating Value (Btu/lb)	14,518	14,397
Viscosity of Fuel @ 100 sec ⁻¹ (Cp)	400	300
Mean Size, micrometers	----	14.1
Dispersant (wt%)	1.2	1.4
Prominate Analysis of Coal (wt%)		
Ash	3.08	3.88
Volatiles	38.49	36.10
Fixed Carbon	58.43	60.02
Ultimate Analysis of Coal (wt%)		
Carbon	84.00	77.14
Oxygen (by difference)	7.81	14.34
Hydrogen	5.63	5.80
Nitrogen	1.64	1.82
Sulfur	0.92	0.90
Forms of Sulfur (Dry Coal Basis)		
Total Sulfur (wt%)	0.92	0.90
Sulfate	0.05	0.04
Pyritic	0.06	0.01
Organic	0.81	0.85

Sulfur content in all three CWM Fuels are approximately 1 wt% on a dry coal, ash free basis. Physical cleaning removed most of the inorganic sulfur, but left behind organic sulfur. A detailed analysis of sulfur forms (Table 1) further indicated that only trace amounts of sulfate (0.05 wt%) and pyritic sulfur (0.01-0.06%) remained in the sample, the majority was organic sulfur (0.80%). The ash contents in the samples range from 1.9 to 2.1 wt% on a fuel basis. The ash composition analysis (Table 2) indicates the acidic mineral properties in the coal fuels. The base-to-acid ratio is 0.28 for A and 0.18 for C, respectively. The relative amount of the basic and acidic constituents in the ash can be used as a means of predicting the ash fusion temperatures and the slag properties.

TABLE 2
Ash Slagging Properties

CWM Batch	A	C
Ash Composition		
SiO ₂	43.40	53.0
Al ₂ O ₃	27.80	28.1
Fe ₂ O ₃	14.10	11.6
CaO	3.33	1.86
MgO	0.816	0.61
Na ₂ O	1.37	0.91
K ₂ O	0.723	1.03
TiO ₂	2.10	2.07
MnO ₂	0.066	0.065
P ₂ O ₅	0.406	0.314
V ₂ O ₅	0.078	0.06
PbO	0.072	0.04
Ash Fusion Temperatures (°F)		
Oxidizing/Reducing		
Initial Deformation	2375/2308	2670/2460
Softening	2700/2543	+2700/2605
Hemispherical	+2700/2565	+2740/2650
Fluid	+2700/2698	+2700/2700
Base/Acid Ratio	0.28	0.18
Silica Ratio	79.6	70.4
Viscosity From Equivalent Silica @ 2600°F (poise)	169	575
T ₂₅₀ Temperature (°F)	2527	2790
Fouling Index	0.38	0.18
Slagging Index	0.26	0.17

RESULTS AND DISCUSSION

The Fate of Sulfur in Slagging Coal Combustion

Upon injecting a coal-water slurry into the primary zone, the coal slurries are atomized and undergo a rapid devolatilization followed by a burnout of the char (Refs. 1,2). Figure 2 illustrates a simplified scheme involved in the combustion of a coal particle. The volatile organic and inorganic sulfur species are vaporized from the burning coal particles and are transported to the surface by molecular diffusion. The reducing atmosphere surrounding a burning particle allows the reduction to take place on volatile species, but as soon as the vapors diffuse away from the burning particle, the oxidizing nature of the bulk gas stream would oxidize sulfur species to their highest oxidation state. The rate of sulfur release from coal is very fast from both sulfur bound in the organic matrix and sulfur in discrete minerals even under the local reducing conditions. Recent thermal analysis (Ref. 3) indicated that catalysis or acceleration of coal combustion occurs by its pyrite impurities due to the fact that FeS_2 promotes self-heating and spontaneous combustion of coal.

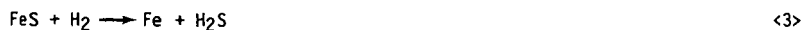
Under rich zone reducing conditions, pyritic sulfur (pyrite or marcasite, FeS_2) decomposes to sulfur (S_2), hydrogen sulfide (H_2S), and carbonyl sulfide (COS) (Ref. 4). Elemental sulfur is given off at 475°C (887°F) from iron disulfide (pyritic sulfur) with accompanying reduction to FeS (Ref. 5):



The rate of this reaction becomes large above 1000°F . In addition, the decomposition of carbon-hydrogen bonds in coal will occur at relatively low temperatures and yield hydrogen for reduction of FeS_2 . Mineral matter such as silicates or basic minerals in coal may catalyze the reduction of FeS_2 (Ref. 6).



and



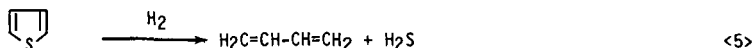
Reaction <2> becomes important above 930°F but reaction <3> is slow even at 1470°F (Ref. 7). The combustion product such as CO can also react with FeS_2 according to:



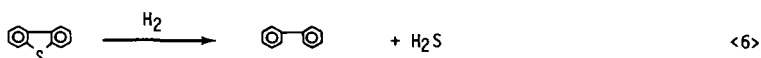
but the reaction is slow below 1470°F (Ref. 7).

The rich zone devolatilization of organic sulfur is not well documented, however, it is believed that hydrogen sulfide (H_2S) is the principal product, accounting for typically 90% of the evolved sulfur, with contributions of COS , CS_2 , and S_2 (Ref. 4). However, these species will turn to higher oxidized states, SO_x , as they are exposed to the primary air stream. Thiophenes represent the dominant organic-sulfur in the coal. Thiophene itself is stable

up to 840°F and dibenzothiophene is stable to at least 1020°F (Ref. 7).
Reduction of thiophene proceeds according to:



and dibenzothiophene reacts according to:



Sulfur release during coal devolatilization can be inhibited by inherent capture by coal-bound mineral matter, particularly calcium oxides and sodium oxides (Refs. 4,8):



In fuel lean flames and oxidizing atmospheres, over 90% of the sulfur is converted to SO_2 while the remaining several percent exist as SO_3 (Ref. 4). Hydrogen sulfide (H_2S) which is originally released from pyritic and organic sulfur in the primary zone is rapidly converted to SO_2 in the lean secondary via the sequence (Ref. 9):



The capture of sulfur dioxide with the calcium-based coal minerals could also occur as



but, calcium sulfate is stable only at temperatures below 2200°F (Ref. 10).

Total sulfur conversion to the oxide is generally high in pulverized coal combustion, the remainder largely combining with the ash. Table 3 compares major compositions between a piece of slag retained in the slag pit of primary zone and ash particulates collected from the exhaust gas. A significant amount of sulfur associated with ash particulates was observed, compared to a trace retained in the slag. A sulfur distribution in coal combustion based on TSSC combustion tests of eastern Kentucky bituminous coal is shown, in Table 4 which up to 91% of sulfur was converted to oxides.

TABLE 3
Composition Analysis (a)

Composition, wt. %	Slag (Primary Zone)	Ash (b) Particulates
SiO ₂	43.7	44.4
Al ₂ O ₃	32.6	22.6
TiO ₂	2.04	2.16
Fe ₂ O ₃	11.6	9.34
CaO	1.72	1.25
MgO	0.70	0.56
SrO	0.22	0.12
K ₂ O	1.07	1.04
Na ₂ O	0.75	1.18
P ₂ O ₅	0.12	0.39
Cr ₂ O ₃	0.08	0.39
CuO	0.02	0.08
MnO ₂	0.10	0.09
NiO	0.09	0.45
PbO	0.03	2.90
V ₂ O ₅	0.05	0.06
SO ₃	0.07	11.3

(a) Using batch 'C' CWM as feed
(b) Carbon-free basis

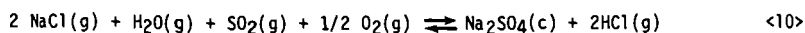
TABLE 4
Sulfur Distribution in Coal Combustion (a)

Total Sulfur in Fuel	Sulfur Out		
	S Adsorbed as Sulfates in Ash Particulates	(b) S Retained in Slag	S Exhausted as SO _x
0.63 lb S/10 ⁶ Btu	0.06 - 0.23	0.001	0.40 - 0.57
100%	9.2 - 36.8%	0.2%	63.0 - 90.6%

(a) Based on an Eastern Kentucky coal having 0.92% wt. S dry coal basis and 8708 Btu/lb CWM where CWM has 60% wt. coal loading (Batch A feed)
(b) Slag based on an average 70% wt. of slag retention.

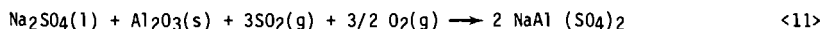
The Effect of Sulfur on Corrosion and Deposition

In combustion, sodium and potassium are likely to be released from coal as the most volatile species, i.e. chloride or hydroxide. However, in a combustion environment at temperatures below about 1800°F, a significant proportion of the vapor alkali will be converted to condensed phase sulfate (Ref. 11).



The estimated residence time required for evaporation of sodium chloride and its conversion to sulfate is about 2 sec. (Ref. 12). Depending on conditions of temperature, pressure, and gas composition, the sulfate could condense onto entrained particulates or nucleate to form an aerosol.

Corrosion could be initiated when the alkali sulfates condense on the metal due to the temperature drop through the turbine and due to the contact with the cooled turbine blades resulting in an increase in alkali sulfate flux to attack the protective oxide (Ref. 13).



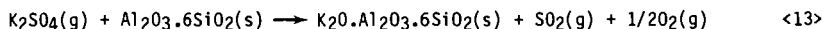
The protective oxide scale (e.g. Al_2O_3) is destroyed and the subsequent reformation is inhibited.

Corrosion may also occur through an increase in the acidic component (SO_3) to react with protective Al_2O_3 scale on steel without the presence of alkali (Ref. 13).



Increased transport of S through the oxide scale will occur and sulfate phase will be formed below the Al_2O_3 scale.

The actual mechanism of corrosion in coal-fired gas turbines is not completely understood. Alkali sulfate vapor released during combustion could partially be adsorbed by the aluminosilicates, inherent coal minerals, which are efficient "getters" for alkali metal sulfates (Refs. 11, 14).



The slag removal feature of a slagging combustor can also greatly reduce the impact of coal corrosive materials. Over 50% of the alkali introduced in coal feed can be expected to be removed as slag in the primary combustion zone (Table 5). The short residence times in gas turbine combustor, and particularly in the hot end zone could further reduce alkali metal vaporization. Thus, a precombustion cleaning of coal in conjunction with unique operating features of the slagging combustor may greatly reduce the corrosion severity potential of coal.

The formation mechanism of deposited matter on turbine blades or vanes is believed to start with molten ash or fly slag sticking to the metal surface. Chemical analyses of the exhaust deposit and the slag (Table 6) indicated that the deposited matter has almost identical chemical compositions as the slag collected in the slag pit. Neither contained any significant amount of sulfur or water-soluble alkali sulfate salts. Petrographically, the two materials were similar except that the exhaust deposit contained gas bubbles. X-ray diffraction and electron microprobe studies showed that the two samples consisted basically of a glass phase containing bladed mullite. A spinel-like phase was seen in the deposit material. The mullite and spinel both probably crystallized during solidification of the melt. It has been speculated recently that alkalis may never escape from the coal aluminosilicate coordination environment (Ref. 4). Based on the decomposition mechanisms of coal alkali minerals (illite) as illustrated in Figure 3, surface moisture and mineral water are desorbed at approximately 300°F (150°C), dehydration

takes place between 890-1100°F at which temperature two water molecules are split off from the four hydroxide units, and somewhere between 1560-1832°F decomposition of the anhydride take place to form spinel ($\text{Al}_2\text{FeMg}_{1.5}\text{O}_6$) and glass ($\text{K}_{1.5}\text{Si}_{6.5}\text{Al}_{1.5}\text{O}_6$). However, at higher temperatures (3000°F), such as slagging conditions, the spinel can redissolve into the melt, and glass phases (e.g. mullite and cristobalite) may be reformed while gaseous alkali species can be released.

CONCLUSIONS

The sulfur content of the coal introduced into the gas turbine combustion system dictates the degree to which sulfur capture compounds or hot-gas cleanup must be utilized. The coal desulfurization to a level acceptable for emissions and corrosion control is a key issue in the development of direct coal-fired gas turbines. Uncontrolled sulfur emissions is a direct function of the sulfur level in the coal and will exceed current NSPS levels. Sulfur compounds in the combustor exhaust also have the potential to cause deposition and corrosion on turbine blades. The availability of naturally occurring low-sulfur coal is limited as is the applicability of coal beneficiation. Physical cleaning will remove most of the inorganic sulfur, but will leave behind organic sulfur. Hot aqueous caustic leaching and molten alkali desulfurization can remove part of the organic sulfur, but appear to be expensive. There is also a potential risk of losing volatile and increasing alkali levels in the feed.

Therefore, in the near-term, sulfur control via sulfur retained in rejected slag and sorbent capture during coal combustion represent important routes for development. Coal beneficiation and post combustion gas clean-up upstream of the turbine are alternatives to in-situ sulfur control in the combustor, although the cost effectiveness of these options is questionable. Introduction of lime or dolomite sorbent for sulfur capture will also impact on ash fusion and deposition as well as on inherent coal mineral "getters" for alkali.

TABLE 5
Slag Retention Properties

Ash or Slag Composition	CWM Batch					
	A			C		
	CWM Feed	Slag	% Removal ^(a) in Slag	CWM Feed	Slag	% Removal ^(b) in Slag
SiO_2	43.40	46.52	75	53.0	48.7	60
Al_2O_3	27.80	28.38	71	28.1	32.6	75
TiO_2	2.10	1.39	45	2.07	2.04	64
Fe_2O_3	14.10	13.71	68	11.6	11.6	65
CaO	3.33	3.54	76	1.86	1.72	60
MgO	0.82	0.47	41	0.61	0.70	74
Na_2O	1.37	1.09	54	0.91	0.75	53
K_2O	0.72	0.54	56	1.03	1.07	67
P_2O_5	0.41	0.27	50	0.31	0.12	25
	94.05	95.91		99.49	99.30	

(a) Based on 70% slag retention from Batch 'A' CWM
(b) Based on 65% slag retention from Batch 'C' CWM

TABLE 6

Comparison of Compositions between Deposited Material and Slag (a)

Composition, wt.%	Deposited Material	Slag
SiO ₂	51.4	52.3
Al ₂ O ₃	29.5	29.2
TiO ₂	1.61	1.53
Fe ₂ O ₃	12.0	11.7
CaO	1.95	1.79
MgO	0.66	0.62
SrO	0.23	0.22
K ₂ O	0.98	0.99
Na ₂ O	0.98	0.96
P ₂ O ₅	0.31	0.13
Cr ₂ O ₃	0.06	0.07
CuO	0.04	0.01
MnO ₂	0.07	0.07
NiO	0.13	0.09
PbO	0.01	0.01
V ₂ O ₅	0.05	0.05
SO ₃	0.07	0.19
Soluble Salts, wt%		
Na ₂ O	0.014	0.010
K ₂ O	0.004	0.003
SO ₃	0.012	0.012

(a) Deposition run using Batch 'C' CWM feed

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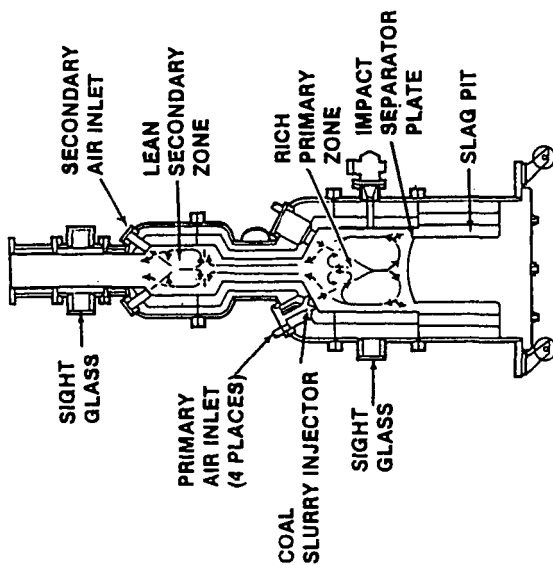


Figure 1. Solar's Two Stage Slagging Combustor

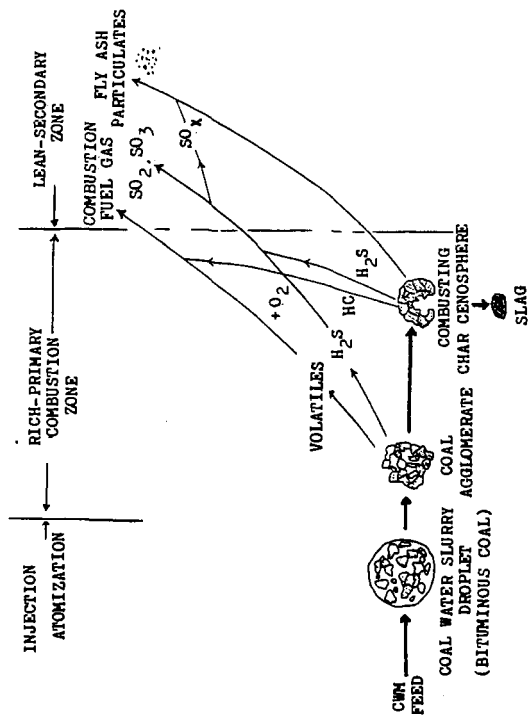


Figure 2. CWM Burnout and Sulfur Routes in Combustion

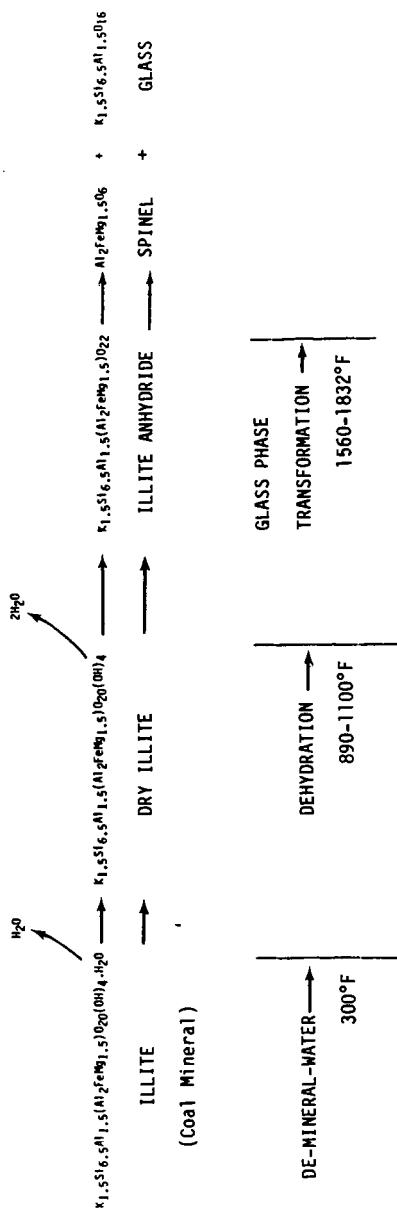


Figure 3. Decomposition Mechanisms of Coal Alkali Mineral